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13. ABSTRACT *(Maximum 200 Words)*

We report observation of holographic surface relief gratings with relatively large amplitude on a second order nonlinear optical polymeric material. Surface relief gratings on these polymer films were created upon exposure to polarized Ar+ laser beams at 488 nm without any subsequent processing steps. The surface structure of the relief gratings was investigated by atomic force microscopy. The depth of the surface relief in a typical case was 140 nm which is approximately 25 % of the original film thickness. Diffraction efficiency of gold-coated gratings were investigated as a function of wavelength and capability of recording orthogonal gratings on the same film was demonstrated.

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by

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Department of Chemistry
Lowell, Massachusetts

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Laser-induced holographic surface relief gratings on nonlinear optical polymer films

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ABSTRACT

We report observation of holographic surface relief gratings with relatively large amplitude on a second order nonlinear optical polymeric material. Surface relief gratings on these polymer films were created upon exposure to polarized Ar^+ laser beams at 488 nm without any subsequent processing steps. The surface structure of the relief gratings was investigated by atomic force microscopy. The depth of the surface relief in a typical case was 140 nm which is approximately 25 % of the original film thickness. Diffraction efficiency of gold-coated gratings were investigated as a function of wavelength and capability of recording orthogonal gratings on the same film was demonstrated.

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Holographic gratings (both surface relief and refractive index) using polymer films have potential applications in optical devices. Holographic gratings on photoresists have been conventionally used to create surface or relief gratings.[1] Such a process usually involves exposure of the photoresist to an interference pattern at a wavelength at which the photoresist responds. After exposure the photoresist is developed (usually by a wet chemical process) followed usually by a baking process. Laser ablation techniques have also been employed to inscribe gratings on polymers, although the residual debris and charring effects due to ablation often result in increased background scattering.[2] Surface relief gratings have been recorded on thermoplastic photoconductor materials as well.[3] In this case, the surface deformations result when charged films are exposed to an interference pattern and heated close to the glass transition temperature (T_g) of the polymer. In this letter we report the direct formation of relatively large amplitude surface relief gratings on polymer films upon exposure to an interference pattern at modest intensities without any subsequent processing steps.

An epoxy-based polymer was utilized in this study. This polymer was synthesized from diglycidyl ether of bisphenol A and 4-(4'-nitrophenylazo) phenyl amine and functionalized with photo-crosslinkable methacryloyl groups.[4] The T_g of this polymer was 102°C. The polymer was soluble in common organic solvents and formed good optical quality films by spin coating. Polymer thin films were prepared by spin coating the filtered 10 wt.% polymer solution in 1,4-dioxane onto microscope glass slides and silicon wafers. These films were dried in a vacuum oven at 60°C overnight. The typical thickness of films was about 0.6 μm. The UV-visible absorption spectra of the spin-coated polymer films showed a maximum at

456 nm. The second order nonlinear optical (NLO) properties and photo-induced orientation of this polymer have extensively been studied by our group.[5,6] This polymer shows large second order NLO effects subsequent to poling and good temporal stability when crosslinked.[5] Birefringence has also been optically induced in this polymer film by polarized light through trans-cis-trans isomerization of the azobenzene groups.[6] The process involves repeated trans-cis photoisomerization of azobenzene groups and thermal cis-trans relaxation resulting in the alignment of azobenzene groups in the direction perpendicular to the polarization of the incident light.[6-9] Therefore, birefringence in films resulting from this alignment of azobenzene groups could be used for producing erasable holographic gratings.

In this study, holographic gratings were recorded by a simple interferometric apparatus[10] at a wavelength of 488 nm from an Ar^+ laser with 70 mW/cm^2 intensity. Gratings with period from 0.5 μm to 2.3 μm have been recorded by adjusting the writing angle. The polarization of two writing beams were selected to be *p* -polarized. Typical recording time was about 10 min. Grating formation was monitored with a low power He-Ne laser at 633 nm by measuring the power of the +1 order diffracted beam in the reflection mode during the writing process. A very strong diffraction of the ambient light was observed from the surface implying the presence of a surface relief grating.

The surface relief structure of the gratings on polymer films were investigated by atomic force microscopy (AFM) before and after the holographic gratings were recorded. As shown in Figure 1 (a), the three-dimensional view of the surface gratings as obtained by AFM measurements showed very regularly spaced surface relief structures with

a period of 0.8 μm. The original film surfaces before exposure to the writing beams were quite smooth and planar with just tens of angstroms fluctuations in the depth without any regular periodicity. The grating spacing could be controlled by changing the angle between two writing beams and was consistent with the theoretically calculated spacing. Thus, clearly the surface relief patterns were produced by the interfering laser beams. Figure 1 (b) shows the AFM surface profile of the same grating along the ripple pattern. The depth of the surface relief patterns was about 140 nm which is approximately 25% of the original film thickness. While irradiation of 488 nm results in reorientation of the azo groups leading to birefringence in the polymer film, such a large surface change on the polymer film is not expected due to the alignment of molecules alone. Large scale molecular motion and volume change due to reorientation seem to be occurring simultaneously. The mechanism leading to the formation of the grating is not well understood at this moment. It is possible that earlier reports of diffraction from birefringent gratings in high T_g azo dye containing polymers may also have a surface grating contribution. The gratings can be erased by heating the sample above T_g. After the gratings were erased, the spectroscopic data showed no evidence of degradation or charring of the polymer films.

To demonstrate the possibility of recording multiple gratings and investigate the corresponding change of the surface structure, two sets of gratings were recorded orthogonally to each other. As shown in Figure 2, the gratings were highly symmetric and identical so the sequence of writing was not distinguishable. The depth of relief patterns was the same as that of the single gratings. This indicates that the effect saturates on long exposure.

Diffraction efficiencies from a surface relief grating were measured at various wavelengths. Figure 3 shows the wavelength dependence of the diffraction efficiency of a grating with a spacing of 1 μm in the reflection mode. The diffraction efficiencies were measured to be in the range of 2 to 5 %. In the transmission mode, diffraction efficiencies at 514 nm as large as 15 % have been measured. The diffraction efficiencies of a gold coated grating were measured at various wavelengths as shown in Figure 4. A thin layer (~50 nm) of gold was deposited on the grating surface by thermal evaporation in vacuum. The gold coating enhanced the diffraction efficiencies of the relief grating with a peak diffraction efficiency of about 30 %. This further confirms that the relief gratings exist on the polymer surface.

In conclusion, we have observed surface relief holographic gratings on polymer films containing an azobenzene NLO chromophore without any subsequent processing steps. Due to the ease with which relief gratings can be recorded on the polymer films, such polymers may have potential applications for optical devices and optical elements. While the manuscript was under preparation we became aware of similar results obtained by Natansohn *et al.* from Queen's university, Kingston, Canada.[11]

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FIGURE CAPTIONS

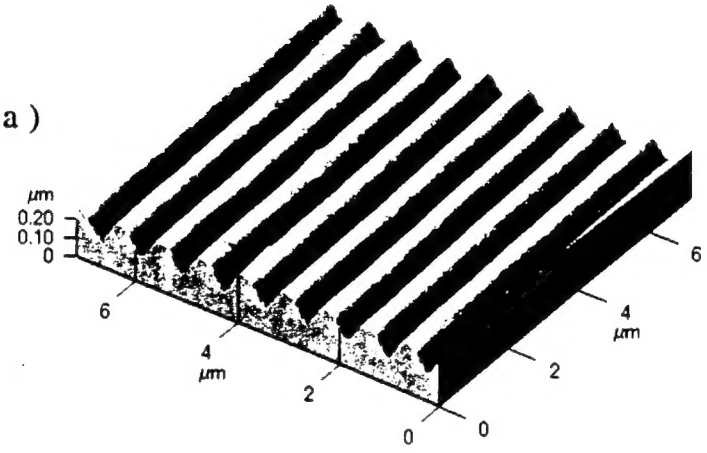
Figure 1. (a) AFM three-dimensional view and (b) surface profile of the grating on the polymer film.

Figure 2. AFM three-dimensional view of two gratings recorded orthogonally to each other.

Figure 3. Diffraction efficiency of the grating in the reflection mode as a function of wavelength of the reading beam.

Figure 4. Diffraction efficiency of the gold coated grating in the reflection mode as a function of wavelength of the reading beam.

(a)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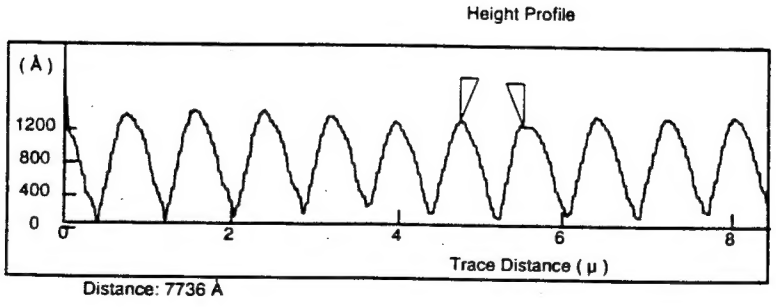
0.10
0
6
4
μm
2
0
0
2
4
μm
6

(b)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(Å)
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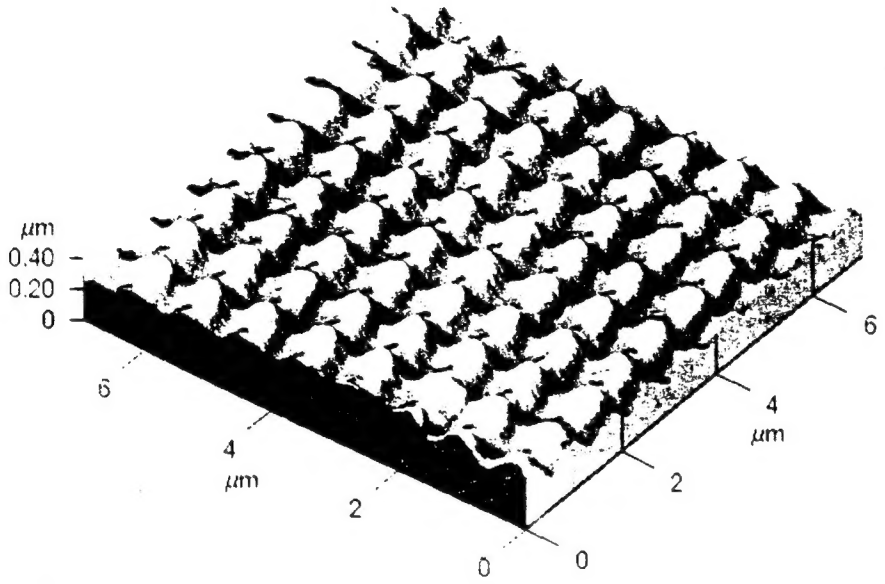
800
400
0
0
2
4
6
8
Trace Distance (μ)
Distance: 7736 Å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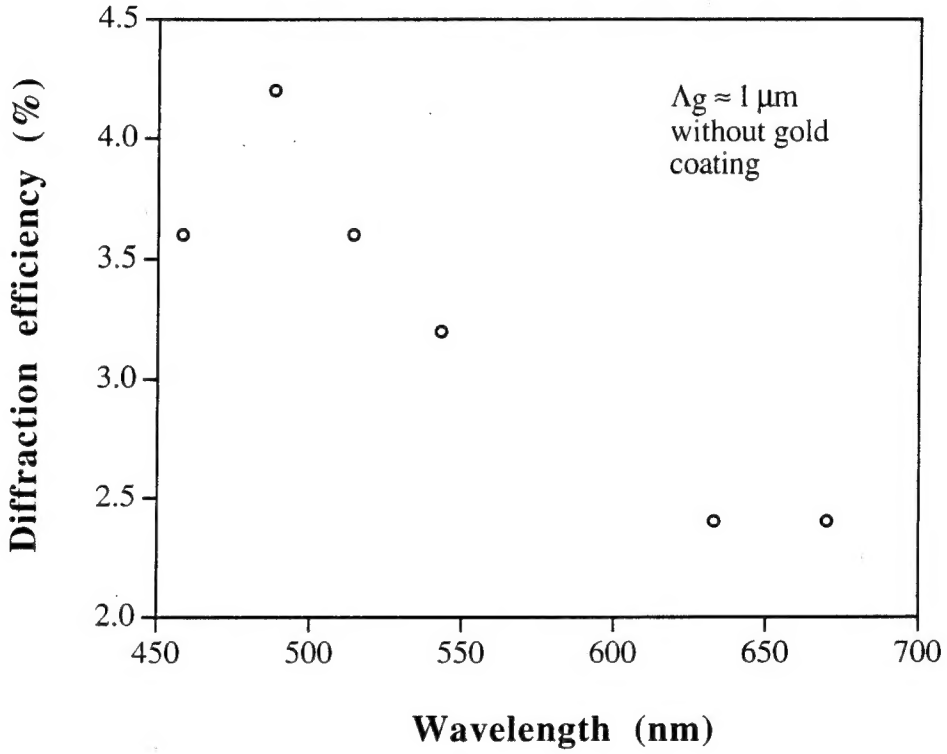
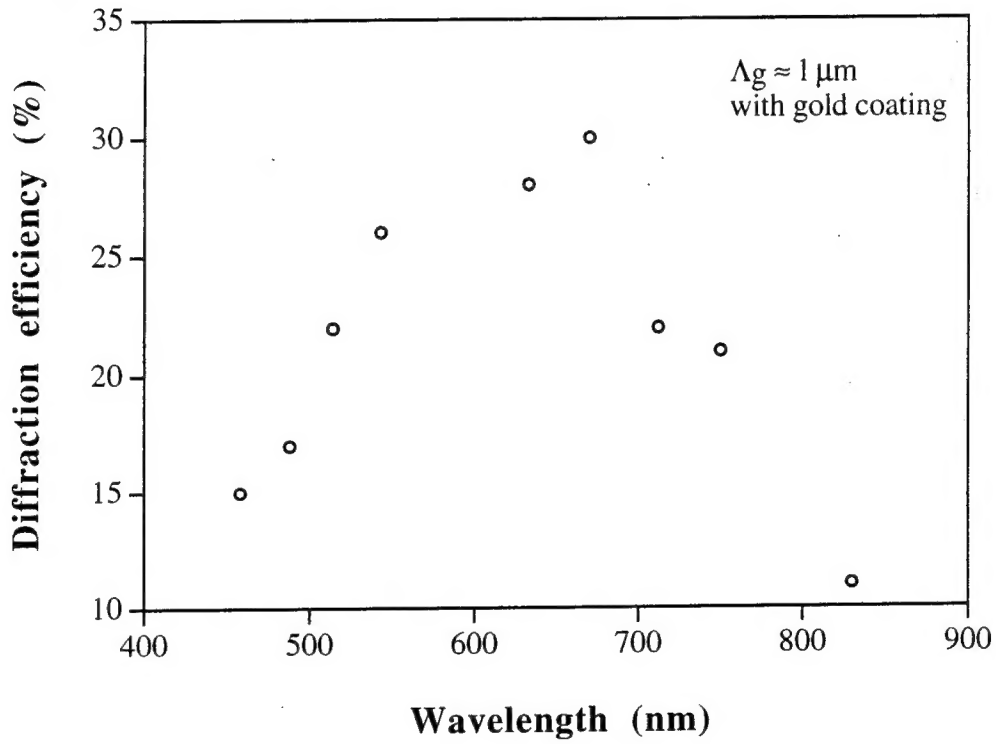
0.20
0
6
4
µm
2
0
0
2
4
µm
6


Diffraction efficiency (%)
4.5
4.0
3.5
3.0
2.5
2.0
450
500
550
600
650
700
Wavelength (nm)
Λg ≈ 1 μm
without gold
coating


Λg ≈ 1 μm
with gold coating
Diffraction efficiency (%)
35
30
25
20
15
10
400
500
600
700
800
900
Wavelength (nm)